(12) UK Patent Application (19) GB (11) 2 217 229 (13) A

(43) Date of A publication 25.10.1989

(21) Application No 8809694.6

(22) Date of filing 25.04.1988

(71) Applicants
Enersolve Chemical Company Limited

(Incorporated in the United Kingdom)

42 Upper Berkeley Street, London, W1H 8AB, United Kingdom

The City University

(Incorporated in the United Kingdom)

Northampton Square, London, EC1V 0HB, United Kingdom

(72) Inventors
Peter Street
Albert Reginald David Thorley

(51) INT CL⁴
B01F 17/00 17/22 17/44

(52) UK CL (Edition J)
B1V VF V107 V108 V109 V205
U1S S1359

(56) Documents cited
None

(58) Field of search
UK CL (Edition J) B1V VB VF
INT CL⁴ B01F

(74) Agent and/or Address for Service
Carpmaels and Ransford
43 Bloomsbury Square, London, WC1A 2RA, United Kingdom

(54) **Solubilising composition**

(57) A solubilising composition allows oil and water, especially diesel oil and water, to be combined as a clear, stable homogenous solution. The composition comprises appropriate amounts of the following components
(a) an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point blow -15°C,
(b) a diethanolamide of a higher fatty acid, or a mixture of such diethanolamides, preferably equal parts by volume of lauric diethanolamide and oleic diethanolamide, and
(c) a polyglycol ether of a higher fatty acid, preferalby ethoxylated oleic acid, and, optionally also ethylene gylcol monobutyl ether. Fuel extenders may also be included in the resulting solution.

GB 2 217 229 A

2217229

SOLUBILISING COMPOSITION

This invention relates to a composition which enables water and oil to be combined into a mixture which behaves as a clear stable homogenous solution. The composition may be used, for example, in forming stable solutions of fuel oils and water and finds particular use as an additive to diesel fuel oil that has previously been contaminated with water or to diesel fuel oil that might be expected subsequently to suffer from such contamination.

The presence of water in, particularly, fuel oil can cause a number of difficulties. If the water is present as an undesired contaminant, the burning of the resultant fuel is often uneven or, if the fuel is used in an engine, erratic running and stalling often results ,together with a serious risk of corrosion. In addition, the presence of water in fuel oils in amounts too small to give rise to such difficulties can still be undesirable as it can produce a lack of clarity or haze which is unappealing to the consumer. On the other hand, there are occasions when it might be desirable to be able deliberately to add water to fuel oils in a stable mixture as an extender and for the known improvements in performance and cleaner exhaust emission that can result in, for example, engines using diesel fuel.

A large number of attempts have been made to deal with these problems by attempting to create stable emulsions of the diesel or other fuel oil with water. Such attempts, even with proprietory brands of additive (diesel fuel improvers), have not been wholly successful because long-term stability of the resulting mix cannot be achieved in practice. As the emulsions or suspensions formed with the addition of such additives break down, problems of poor engine

running, even stalling, and corrosion of system components (including biologically aggravated corrosion) arise. Stability problems have been found to be particularly acute with the higher fraction distillate hydrocarbon fuels (such as gasolene, kerosene and normal diesel fuels) in which separation of the oil and water components often occurs in a very short period of time. Where biocides are added to the emulsion to combat biochemically aggravated corrosion, this adds more complications to the already difficult task of attempting to formulate fuel additives for the stable mixing of oil and water.

The present invention seeks to avoid the above mentioned problems and to provide additives which allow the formation of oil-water mixtures which are true solutions or behave as such. The term "solution" herein thus includes any mixtures which are clear, homogeneous and have substantially the same stability as solutions.

The present invention accordingly provides a composition for combining oil and water as a stable solution which comprises (a) an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15° C, (b) a diethanolamide of a higher fatty acid, or a mixture of such diethanolamides and (c) a polyglycol ether of a higher fatty acid.

The components of the composition are appropriately mixed together (with the alcohol ethoxylate as the major component) in amounts which would allow a solution to be formed on addition to the intended oil and water mixture. The mentioned higher fatty acids include the normal emulsifier-forming acids, of which lauric and oleic acid are particularly preferred.

Particularly preferred compositions of the invention comprise the following components

(1) 48 parts by volume of an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15°C,

(2) 3-8 parts by volume of lauric diethanolamide,

(3) 3-8 parts by volume of oleic diethanolamide,

(4) 1.5-4 parts by volume of a polyglycol ether of a higher fatty acid, e.g. ethoxylated oleic acid,

the parts by volume in each case being relative to the total volume of the composition.

In an alternative embodiment components (2) and (3) are replaced by 6 to 16 parts by volume of either lauric diethanolamine or oleic diethanolamine alone.

The composition according to the invention preferably also includes 0.25 to 1 part by volume of ethylene glycol monobutyl ether as an extra component. The presence of this extra component is particularly useful in dealing with mixtures of water and lighter fraction oils.

The present invention further provides a method of forming a stable solution of an oil and water mixture comprising adding to the oil and water mixture a composition of the invention in an amount sufficient to provide a clear stable solution on mixing, and such a solution when so produced.

The number of parts by volume of each component in the composition is selected so as to allow for the

formation of a stable solution of the intended oil and water mixture. The exact amounts of each component of the composition required to give a solution of the intended oil-water combination may easily be found by simple experiment.

As an example, if a 10 parts by water of water in 100 parts by volume of normal diesel oil is to be treated, an appropriate composition would comprise 48 parts of component (1), 8 parts each of components (2) and (3), four parts of component (4) and 1 part of the ethylene glycol monobutyl ether. Where there is a lower amount of water present, lesser proportions of components (2) to (4) would normally be present in the composition. For example, if 1 part by volume of water in 100 parts by volume of diesel is to be treated, an appropriate composition would comprise 48 parts of component (1), 3 parts of components (2) and (3), 1.5 parts of component (4) and 0.25 parts of the ethylene glycol monobutyl ether.

The minimum quantity of composition to be added would normally be expected to be between 5 and 15 parts by volume relative to the volume of the oil water mixture to be treated, but the exact amount may be found by gradually mixing in the composition until a clear solution is formed. Thus, for example, 10-12 parts of the agent (but preferably 16 parts for the best effect) are sufficient to treat the 10 parts water : 100 parts diesel mixture already mentioned, whereas 6 parts by volume per 100 parts of mixture are suitable for treating the 1 part water : 100 parts diesel mixture. The addition of too low a quantity of composition to the oil and water mixture (as for example only 2 parts of composition to the first mentioned water: diesel mixture) is to be avoided as it will result in just an emulsion being formed instead of a solution.

The components of the composition are all readily available commercially. Suitable alcohol ethoxylates of component(1) are for example "Dobanol 91/2.5" (Trade Mark of Shell Chemicals) and "Synperonic 91/2.5" or "Synperonic A 3" (Trade Marks of I.C.I. Plc.). "Texofor M-6" (Trade Mark of ABM.Limited) is suitable as the polyglycol ether of higher fatty acids of component(4).

Particularly preferred ethoxylates of component (1) are those based on C_9 and C_{11} alcohols mixtures, more especially mixtures also including alcohols having chains with even numbers of carbon atoms.

"Dobanol 91/2.5" is such an ethoxylate obtained by the addition of 2.5 moles of ethylene oxide per mole of Dobanol 91 (a mixture of C_9, C_{10} and C_{11} alcohols).

The less highly preferred "Synperonic 91" range is manufactured by the base catalysed ethoxylation of Synprol 91 - a fully saturated synthetic primary alcohol which contains only C_9 and C_{11} alkyl chains and typically consists of 50% w/w linear alcohols with the remainder being monobranched and predominantly the 2-methyl isomer.

The composition of the present invention not only allows ready mixing of fuel oils and water but also allows the addition of further substances as fuel extenders in the oil-water solution. Thus, for example, animal and vegetable oils, even including tallow and butter, may be added successfully to diesel oil and water to form a clear solution on addition of the composition of this invention.

Other extenders which contain water or are hygroscopic, such as alcohols, may also be

successfully added to fuel oils to form permanent mixtures with the fuel oil. Previous attempts to extend fuel with alcohols, for example, have not been wholly successful because of phase separation and subsequent burning out of valves in the engine by the resulting pure alcohol component.

The compositions of the present invention allow the formation of stable solutions which show no sign of breaking down after extended periods of time, in contrast with the emulsions formed with prior art additives. Thus oil and water mixtures incorporating compositions of the invention have formed clear solutions showing no sign of separation of the components over periods of as long as three years.

The uses of solubilising compositions are by no means restricted to these uses but include numerous other applications such as oil recovery, the safe cleansing under pressure of oil tanks (conventional low-flash point solvents being unnecessary) and as additives to jet fuel. however yet further applications will readily occur to the man skilled in the art.

The following examples illustrate the formation of compositions of the invention and their use for the formation of stable solutions of water and oil and also show that such solutions (in contrast to emulsions formed with conventional additives) have no significant corrosive effect on the various materials employed as fuel system and engine components.

Example 1

A composition suitable for combining 100 parts of diesel with 10 parts of water by volume was prepared by adding together the following surfactants in the volume proportions stated:

240 parts Dobanol 91/2.5
40 parts lauric diethanolamide
40 parts oleic diethanol amide
20 parts ethoxylated oleic acid (e.g. Texofor M6)
5 parts ethylene glycol monobutyl ether

The surfactants were mixed vigorously together to form a homogeneous solution.

The following Example shows the use of this composition for forming a solution of a 10:1 by volume mix of diesel and water.

Example 2

10 ml of water was added to 100 ml of diesel in a clear glass container. The composition of Example 1 was introduced into the resulting diesel-water mixture using a syringe, or an accurately calibrated measuring cylinder capable of holding 15 to 20 ml, and the mixture was stirred slowly until a clear homogeneous solution was created. A good degree of clarity was achieved after some 10 to 12 ml of the composition of Example 1 had been introduced. The remaining bloom was removed, when desired, by the further addition of up to 4 ml of the composition.

The composition according to the invention may equally be formed *in situ* when forming the oil-water solution, as will be seen from the following Examples 3 and 4.

Example 3

A clear solution of diesel oil and water having a volume ratio of 10:1 was formed by combining 100 ml diesel oil and 10 ml water in a suitable transparent glass container and thereafter adding thereto a mixture of 6 ml "Dobanol 91/2.5" and 2 ml oleic diethanolamide and stirring slightly. The solution resulting cleared to a smokey haze. Next a mixture of 1 ml ethoxylated oleic acid "Texofor M6" and 0.25 ethylene glycol monobutyl ether was stirred in.

In a second step, a mixture of "Dobanol 91/2.5" and oleic diethanolamide in a volume ratio of 3:1 continued to be added, stirring gently, until a clear solution was achieved. Not more than 6 ml of "Dobanol 91/2.5" and 2 ml of oleic diethanolamide provided by this latter mixture was normally required - the precise amount depending on their age and quality.

As an alternative, the oleic diethanol amide could be replaced, in part or in whole, by lauric diethanolamide.

Example 4

A clear solution of diesel oil and water having a volume ratio of 100:1 was formed in an identical manner to that of Example 3 except that 3 ml "Dobanol 91/2.5", 0.3 ml oleic diethanolamide, 0.15 ml "Texofor M6" and a few drops of ethylene glycol monobutyl ether were employed in the first step and a mixture of "Dobanol 91/2.5" and lauric diethanolamide in a volume ratio of about 6:1 normally providing not more than 2 ml of "Dobanol 91/2.5" and 0.3 ml of lauric diethanolamide was employed in the second step.

The of amounts of solubilising composition which need to be added to particular oil and water mixtures to obtain a solution may be determined in a similar manner to that shown in the following Example.

Example 5

3 ml of water were mixed with 30 ml of diesel oil. Thereafter 1, 2, 3, 4, 5 and 6 ml portion of the composition of Example 1 were added to separate sample of the oil:water mixture. The results shown in Table 1 were obtained.

Table 1

Content of composition of Example 1	Effect on the diesel oil:water mixture
1 ml	A white substance resembling white gloss paint formed which settled to the bottom of the container. The bulk of the liquid was a semi-clear red.
2 ml	An emulsion with an appearance similar to creme shampoo was formed. This emulsion appeared relatively stable. After 3 weeks it had, however, separated into four layers.
3ml	A reddish solution with a blue haze to it was formed. Even after 3 weeks this solution remained stable with no visible separate occurring.
4ml	A clear diesel-red solution was obtained with no haze and no separation of fluid occurring.

Table 1 (cont'd.)

Content of composition of Example 1	Effect on the diesel oil:water mixture
5 ml 6 ml	No further improvement could be made to the solution containing 4 ml of the composition of Example 1. A similar clear diesel-red solution was obtained using these quantities of the composition although these solutions turned very slightly cloudy after standing for 3 weeks.

The foregoing Table thus shows that the addition of just 9% by volume of the composition is sufficient to allow a solution of the 10:1 diesel:water mixture to be formed. The addition of amounts of composition in excess of 12% by volume may be seen to give no further benefit.

The effectiveness of compositions of the invention as compared with that of proprietary diesel fuel improvers which are claimed to absorb moisture in vehicle fuel systems is shown in the following Example.

Example 6

The composition of Example 1 and other proprietary diesel fuel improvers were compared by adding 10% water to the composition and improvers and vigorously shaking the samples to distribute the water. The specimens were then left to stand.

When the water was added to the composition of Example 1 a reaction was seen to occur immediately. The other diesel fuel improvers, although appearing slightly cloudy when vigorously shaken, very quickly separated into two layers. The composition of Example 1 remained a homogeneous clear pale yellow

liquid even after standing. A piece of mild steel was inserted into each sample. Although this gave no reaction with the mixture of water and the composition of the Example, considerable corrosion occurred in the steel in the other fuel improver samples showing the presence of a separate water phase.

Further investigation showed that the diesel fuel improvers failed to absorb even 0.5% water in diesel.

The compositions of the invention (in pure form and in an oil:water solution) show slight or no corrosive effect on the standard component materials of engines and fuels systems, as may be seen from the following Examples 7 and 8.

Example 7

Samples of the test materials listed in the following Table were each carefully cleaned using emery cloth in the case of metallic samples and tissue in the case of non-metallic samples. A separate jar was provided for each sample in the case of each of the three fluids. The respective jars were then filled with test fluids which were (a) untreated diesel oil, (b) the pure composition of Example 1 and (c) a solution consisting of 30 ml of diesel oil, 3 ml of water and 4 ml of the composition of Example 1 (referred to in Table 2 as "Solution-S1"). Next cleaned samples were immersed in the test fluid in the jars which were left undisturbed at room temperature (20°C) for two months. Table 2 records the visual changes which were noted after this time.

Table 2

Test Material	Rubber	Bundy tube	Reinforced nylon tubing	Copper	Brass	Dural aluminium alloy	Cold-drawn steel tube	Structural steel
Effect on Fluid								
(1) Untreated Diesel Oil	-	-	-	-	-	-	-	-
(2) Solution S1	-	-	-	separation into three layers	discoloured (dark black haze at base)	-	-	-
(3) Pure Additive of Example 1	-	-	-	discoloured (pale green)	green wisps at top of sample	-	-	-
Effect on Test Material								
(1) Untreated Diesel Oil	-	-	Colour of fluid	-	blackened	-	-	slightly tinted brown
(2) Solution S1	size expanded	-	slightly opaque	darkened	"	slight gold tint	-	" "
(3) Pure Additive of Example 1	-	-	Colour of fluid	etched dull pink	"	-	-	" "

- = no visible change

Separate tests show the rubber sample to increase in weight on contact even with untreated diesel. Hence the type of rubber tested would obviously be unreliable in diesel systems.

The noted reaction on copper and brass may be only a surface coating but, in any case, it is anticipated that neutralisation or at least a reduction in the alkalinity in other forms of the solubilising composition may reduce or remove this effect.

Example 8

Since tank corrosion is usually initiated at the interface between the liquid and the air above, a test was set up to simulate conditions in a fuel tank.

Narrow strips of mild steel were placed in bottles half-filled with test fluids, the solution of Example 7, untreated diesel, water and in addition, an emulsion formed by adding only 2 parts of the composition of Example 1 to 30 parts of diesel and 3 parts of water. One set of these four bottles was left undisturbed, another was inverted once and then left undisturbed and a third set was inverted daily. The tops of the bottles were loosened to allow air into the bottles and the effects of corrosion were observed.

The only liquid sample to show any sign of corroding the steel in any of the sets of bottles was water. The emulsion and solution both left the steel perfectly clean, as did the untreated diesel.

The following Example shows that compositions of the invention when added to diesel fuel allow the fuel to be used effectively in engines with possible cost saving from the presence of water or other additives as fuel extenders.

Example 9

A series of tests were conducted on a "Ricardo E6" (Trade Mark) single cylinder four stroke compression-ignition engine in which the compression ratio was set at approximately 22 : 1 and the injection timing was set at 35° before T.D.C. (except for two spot checks of the effects of varying this, which were made in one test at 25 00 rev/min).

A first set of tests was carried out at a constant engine speed of 1500 rev/min to obtain engine torque as a function of pump rack (i.e. throttle) setting. Except in the region of full throttle opening the torque output at a given throttle setting (and hence fuel consumption rate) from a normal diesel fuel was found to be higher than when the composition of Example 1 was added to take a 10:1 diesel:water mix into a fuel solution. Expressed another way - to obtain a given torque, and hence power output, with the fuel solution it was found to be necessary on this test engine, at 1500 rev/min, at low powers, to increase the throttle opening slightly, to compensate for there being less diesel fuel in the total liquid flowrate.

Next a second set of tests enabled performance curves of net load or torque at nearly full throttle to be generated as a function of engine speed in the range 800 - 3000 rev/min by adjusting the load on the torque dynamometer whilst maintaining a constant throttle rack setting.

At engine speeds below about 1600 rev/min the above-mentioned solution provided a greater power output than normal uncontaminated diesel. From 1600 rev/min up to around 2100 rev/min the position was reversed with normal diesel apparently being slightly better, and above this speed normal diesel fuel was considerably better.

However, these tests were conducted at a constant injection timing. Spot tests at 2500 rev/min with both normal diesel fuel and the solution of the diesel:water mix indicated that performance would be improved by advancing the injection timing and also that a greater improvement occurred with the fuel solution. If injection timing could be optimised over the speed range it is anticipated that the benefits of improved performance at this throttle setting should be extended to a speed rather higher than 1600 rev/min.

This Example thus shows that under certain conditions (at least) or with certain types of engines diesel fuel which has been contaminated with 10% tap water and to which the composition of the invention is added to form a solution yields essentially the same, and perhaps slightly improved, power output as a normal uncontaminated diesel fuel oil. It has also been found to be possible to run an engine on diesel fuel oil to which had been added 18% by volume of butter and sufficient of the composition of Example 1 to form a solution.

CLAIMS

1. A composition for combining oil and water as a stable solution which comprises

(a) an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and melting point below -15°C,

(b) a diethanolamide of a higher fatty acid, or a mixture of such diethanolamides, and

(c) a polyglycol ether of a higher fatty acid.

2. A composition according to claim 1, which comprises the following components

(1) 48 parts by volume of an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15°C,

(2) 3-8 parts by volume of lauric diethanolamide,

(3) 3-8 parts by volume of oleic diethanolamide,

(4) 1.5-4 parts by volume of a polyglycol ether of a higher fatty acid,

the parts by volume in each case being relative to the total volume of the composition.

3. A composition according to claim 2, additionally comprising 0.25 to 1 part by volume, relative to the total volume of the composition, of ethylene glycol monobutyl ether.

4. A composition according to claim 3 for combining 10 parts by volume of water in 100 parts by volume of diesel oil, comprising 48 parts by volume of the ethoxylate of component (1), 8 parts by volume of

each of the diethanolamides of components (2) and (3), 4 parts by volume of the ether of component (4) and 1 part by volume of ethylene glycol monobutyl ether, the parts by volume being relative to the total volume of the composition.

5. A composition according to claim 3 for combining 1 part by volume of water in 100 parts by volume of diesel oil, comprising 48 parts by volume of the ethoxylate of component (1), 3 parts by volume of each of the diethanolamides of components (2) and (3), 1.5 parts by volume of the ether of component (4) and 0.25 parts by volume of ethylene glycol monobutyl ether, the parts by volume being relative to the total volume of the composition.

6. A method of forming a solution of a mixture of oil and water comprising adding a composition according to any of claims 1 to 5, to the oil and water mixture in an amount sufficient to provide a clear solution on mixing.

7. A method according to claim 6, in which a composition according to claim 3 is added to a mixture of 10 parts by volume of water and 100 parts by volume of diesel oil in an amount of 14 parts by volume relative to the oil and water mixture.

8. A method according to claim 6, in which a composition according to claim 5 is added to a mixture of 1 part by volume of water and 100 parts by volume of diesel oil in an amount of 6 parts by volume relative to the oil and water mixture.

9. A solution whenever produced by the process of any of claims 6 to 8.

10. A solution according to claim 9, additionally containing a fuel extender.

11. A solution according to claim 10, in which the fuel extender is ethanol, tallow, butter or a vegetable oil.

Published 1989 at The Patent Office, State House, 66/71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office. Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD. Printed by Multiplex techniques ltd, St Mary Cray, Kent, Con. 1/87